Synthesis of *N*,*N*′-bis(9-phenylxanthen-9-yl)ethylenediamine and an investigation of its host–guest inclusion potential

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The novel amine, *N*,*N*′-bis(9-phenylxanthen-9-yl)ethylenediamine **1**, was synthesized by treating 9-phenylxanthen-9-ylium perchlorate with ethylenediamine. Its host potential was assessed by allowing it to crystallise from a range of organic solvents (single and binary mixtures), of which several were found to be included. The stoichiometries of these host–guest complexes were determined through ^{1}H-NMR analysis and their stabilities assessed through thermal analysis. Single crystal X-ray crystallography was used to elucidate the crystal structure of the 1 : 1 **1**·THF inclusion complex. It was found that only one of the two amine moieties of the host functions as a donor, forming a nearly linear hydrogen bond to the oxygen atom of the guest molecule. Each THF molecule is effectively surrounded by host molecules so that the THF molecules are found to occupy discrete "cavities" within the host lattice. The activation energy associated with desolvation of the **1**·THF complex was determined through thermal analysis and was found to decrease as desolvation progressed.

Introduction

There is currently much interest in organic host–guest inclusion chemistry. Apart from the potential practical applications, studies in this field also serve to improve our understanding of the intermolecular forces which play roles in molecular recognition phenomena.[1,2] It has become evident that certain molecular structural elements are desirable for compounds to function effectively as hosts. Included among them are rigidity, the presence of bulky hydrophobic units (such as aryl systems) and hydrogen-bonding capabilities. Certain symmetry features are frequently also important. Clearly, chirality would be a prerequisite for any compound to function as an enantioselective host.

In their work on potential host compounds, Weber *et al.*[3] have studied triaryl methyl derivatives, including examples where two of the aryl rings are bridged together. This family of compounds has proved to be very effective at forming inclusion compounds with numerous organic guest molecules. Another common feature that many members of this host family display is the presence of a hydroxy group, which appears to facilitate complex formation through hydrogen bonding with guest molecules as well as between host molecules. The importance of the hydroxy group in host compounds of this type has also been noted by other workers.[2,4]

The objective of our study has been to determine the effect that replacing the hydroxy group in such systems with an amine moiety would have on their inclusion capabilities. We now report on the synthesis of the novel diamine **1** obtained by reacting ethylenediamine with 9-phenylxanthen-9-ylium perchlorate, and describe an assessment of its potential as a host compound. In addition, the structural features and thermal characteristics of the 1 : 1 inclusion complex it forms with tetrahydrofuran have been elucidated in some detail.

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Experimental

General methods

Melting points were recorded on an Electrothermal IA9000 Series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier Transform Infrared Spectrometer and ^{1}H-NMR and ^{13}C-NMR spectra on a Varian Gemini 200 MHz Spectrometer. Differential scanning calorimetry (DSC) experiments were performed on a Du Pont 910 Standard DSC module, connected to a Du Pont 9000 Thermal Analyser. High purity nitrogen gas was used as purge gas. A heating rate of 5 °C min^{-1} was applied. Compounds were sealed in aluminium DSC pans and their lids pierced, while an empty aluminium pan served as a reference. Thermogravimetric (TG) analyses were conducted on a TGA 51 instrument with Thermo Analyst 2000 (TA Instruments) and the compounds were placed on platinum pans.

Synthesis of *N*,*N*′-bis(9-phenylxanthen-9-yl)ethylenediamine 1

9-Phenylxanthen-9-ol. This compound was synthesised according to a published procedure.[3] The resulting crude material was recrystallised from benzene–petroleum ether to afford 9-phenylxanthen-9-ol (55% yield) as a white powder, mp 160–162 °C (lit.,[3] mp 159 °C) (Found: C, 83.0; H, 5.0. Calc. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1%); $\nu_{max}(CHCl_3)$/cm^{-1} 3588 (free OH), 3380 (br, H-bonded OH) and 1602 (Ar); $\delta_H(CDCl_3)$ 2.73 (1H, s, OH) and 7.00–7.90 (13H, m, Ar); $\delta_C(CDCl_3)$ 72.46 (PhCOH), 118.45 (Ar), 125.60 (Ar), 128.27 (Ar), 128.78 (Ar), 129.25 (quaternary Ar), 130.02 (Ar), 131.09 (Ar), 150.05 (quaternary Ar) and 151.71 (quaternary Ar); *m*/*z* 274 (M^+, 9.2%), 77 (M − 197, 7.6%), 181 (M − 93, 5.4%), 197 (M − 77, 100%) and 257 (M − 17, 13.5%).

***N*,*N*′-Bis(9-phenylxanthen-9-yl)ethylenediamine 1.** 9-Phenylxanthen-9-ol was treated with perchloric acid as described by Taljaard and co-workers,[5] and the resulting 9-phenylxanthen-9-ylium perchlorate (1.00 g, 2.80 mmol) dissolved in dichloro-

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Table 1 Inclusion complexes formed by the host **1** with host : guest stoichiometries and their thermal properties

Guest	Stoichiometry	T_{on}/°C	T_b/°C	(T_{on} − T_b)/°C	Host **1** mp/°C
Acetone	1 : 1	57	56.5	+0.5	211
MeCN	1 : 1	79	80.5	−1.5	206
$MeNO_2$	2 : 1	75	101.2	−26.2	208
THF	1 : 1	74	66	+8	207
Dioxane	4 : 3	115	101.1	+13.9	208
Piperidine	2 : 1	67	106	−39	209
Pyridine	2 : 1	43	115.5	−72.5	211
Ether	2 : 1	80	34.5	+45.5	211

methane (35 ml) before being added to a stirred solution of ethylenediamine (1.74 g, 29.0 mmol) in ether (17 ml) at room temperature. After stirring for a further 30 min, the solution was washed with water (3 × 100 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was recrystallised from chloroform–petroleum ether to give *N*,*N*′-bis(9-phenylxanthen-9-yl)ethylenediamine **1** as a white solid (0.47 g, 0.82 mmol, 59%), mp 204–206 °C (decomp.) (Found: C, 84.0; H, 5.7; N, 4.7. $C_{40}H_{32}N_2O_2$ requires C, 83.9; H, 5.6; N, 4.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600–3300 (NH) and 1601 (Ar); $\delta_H(CDCl_3)$ 2.23 (4H, s, CH_2CH_2), 2.30 (2H, s, NH) and 6.90–7.70 (26H, m, Ar); $\delta_C(CDCl_3)$ 45.43 (CH_2CH_2), 61.92 (PhCNH), 118.17 (Ar), 125.28 (Ar), 127.73 (quaternary Ar), 128.51 (Ar), 129.21 (Ar), 130.02 (Ar), 130.18 (Ar), 131.02 (Ar), 151.90 (quaternary Ar) and 153.30 (quaternary Ar); *m*/*z* 572 (M^+, 0.0%), 181 (M − 391, 59.9%), 196 (M − 376, 23.7%) and 257 (M − 315, 100%).

Assessment of the host potential of 1

Formation of inclusion complexes. *N*,*N*′-Bis(9-phenylxanthen-9-yl)ethylenediamine **1** was recrystallised from a range of organic solvents by dissolution in excess solvent, which was then allowed to evaporate slowly under ambient conditions. The resulting crystals were washed with methanol‡ and dried by suction filtration. ^{1}H-NMR spectroscopy was used to ascertain whether any inclusion of the solvent had occurred and where appropriate, to determine host : guest stoichiometries (Table 1).

Thermal analyses. Those complexes which formed successfully were characterised further using differential scanning calorimetry and thermal gravimetry. DSC traces were obtained for all of these complexes in order to determine their relative thermal stabilities, with Fig. 1 (obtained for the **1**·THF complex) being a representative example. The DSC traces provided the onset temperatures (T_{on}) for the release of the guest compounds from the host. These values, as well as the boiling points of the pure guest compounds (T_b), are given in Table 1. Also calculated for each complex was (T_{on} − T_b) which has been proposed previously as a measure of the strength of enclathration of the guest by the host.[6–8] The stoichiometry of the **1**·THF complex was confirmed by TGA (Fig. 2); the theoretical mass loss for a 1 : 1 complex is 11.18%, while an experimental value of 10.39% was obtained.

Competition experiments. The host **1** was dissolved through heating in an equimolar mixture of two selected solvents, both of which had previously been shown to be included independently by **1**. The solution was then cooled to 0 °C and the resulting crystals filtered, rinsed with methanol, dried and analysed by ^{1}H-NMR spectroscopy. The stoichiometries of the host–guest complexes are given in Table 2.

‡ There was no evidence from ^{1}H-NMR spectroscopy that washing the complexes with methanol led to its inclusion. Even recrystallisation of the host **1** from methanol did not result in inclusion.

Table 2 Competition experiments involving host **1**

Guest I (GI)	Guest II (GII)	Host **1** : GI : GII ratio	Host **1** : (GI + GII) ratio
THF	Acetone	1 : 0.27 : 0.48	1 : 0.75
Dioxane	THF	1 : 0.43 : 0.07	1 : 0.5
Pyridine	Ether	1 : 0 : 0	1 : 0
Piperidine	Pyridine	1 : 0.31 : 0	1 : 0.31

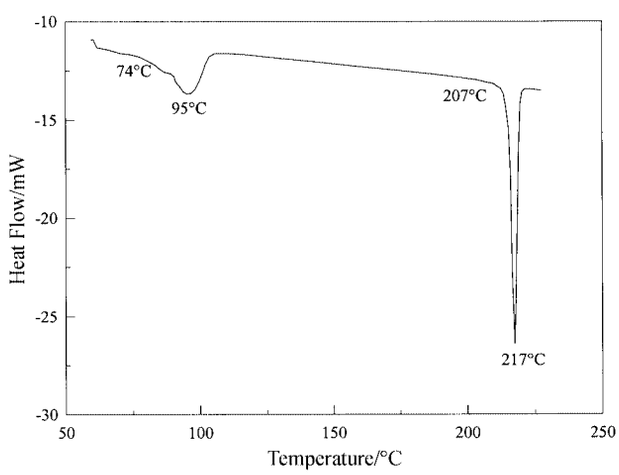


Fig. 1 Host **1**·THF DSC trace.

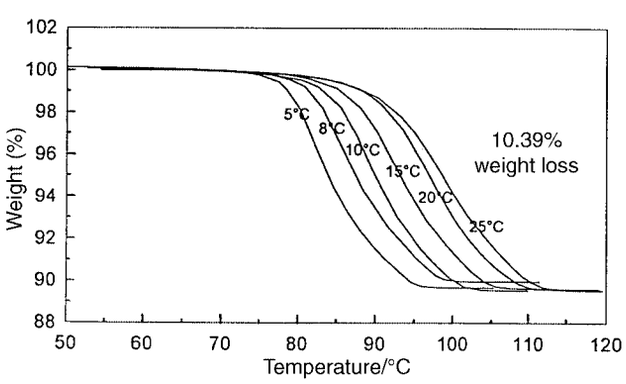


Fig. 2 TG traces for the **1**·THF complex heated at 5, 8, 10, 15, 20 and 25 °C per minute.

Elemental analysis of the 1·THF complex. The stoichiometry of the **1**·THF complex was confirmed by elemental analysis (a 1 : 1 complex requires C, 81.96; H, 6.25 and N, 4.34%. C, 81.68; H, 6.08 and N, 4.13% were obtained).

Single crystal X-ray crystallographic analysis of the 1·THF complex. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα-radiation ($\lambda = 0.7107$ Å) with the crystal moderately cooled by a nitrogen stream from an Oxford Cryosystems cooling system to enhance diffraction

Table 3 Crystallographic data for **1**·THF

Chemical formula	$C_{40}H_{32}N_2O_2{\cdot}C_4H_8O$
Formula weight	644.81
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
μ(Mo-Kα)/mm^{-1}	0.078
$R(F)$, $F > 4\sigma(F)$	0.051
$wR(F^2)$	0.147
S	0.945
a/Å	9.525(2)
b/Å	14.705(3)
c/Å	24.448(5)
V/Å^3	3424(1)
T/K	243(1)
Z	4
Measured data	3428
Unique data	3398
R_{int}	0.0

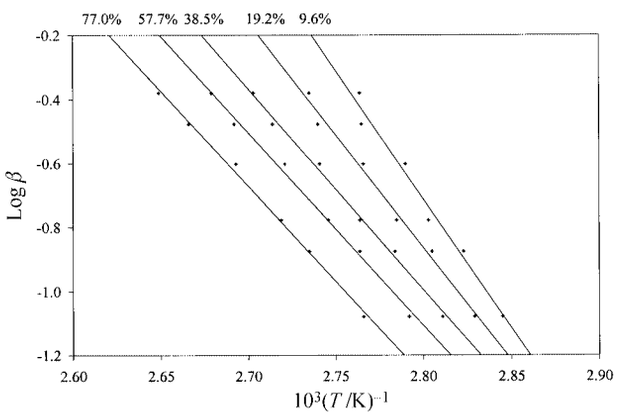


Fig. 3 Plot of log β against $1/T$ at 9.6, 19.2, 38.5, 57.7 and 77.0% of the total mass loss observed.

data quality. The structure was solved by direct methods using program SHELX-86[9] and refined on F^2 with program SHELXL-97[10] which was also used to calculate molecular parameters. Molecular drawings were made with PLUTO.[11] Table 3 lists relevant crystallographic data. CCDC reference number 188/224. See http://www.rsc.org/suppdata/p2/a9/a907232b for crystallographic files in .cif format.

Kinetics of guest release from the 1·THF complex. The activation energy (E_a) of the guest release process for the **1**·THF complex was determined by thermogravimetrically measuring the mass loss it experienced as a function of different heating rates[7] (*e.g.*, see Fig. 2). Plotting the logarithms of the heating rates (β) against the reciprocals of temperatures (in K) recorded at a range of selected fixed percentages of the total mass loss observed gave a series of straight lines (Fig. 3). It has been shown[12] that the slope of such a line approximates $-0.457E_a/R$ (where the gas constant $R = 8.314$ J mol^{-1} K^{-1}), from which the activation energy may be calculated (Table 4).

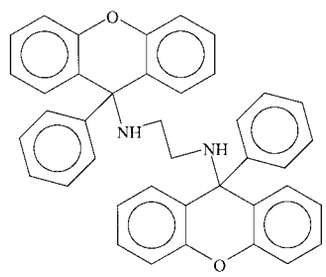
Results and discussion

Our original objective in functionalising 9-phenylxanthene with ethylenediamine had been to synthesize the mono-substituted diamine **2**. However, the only product obtained was the novel *N*,*N*′-disubstituted diamine **1**, even when 9-phenylxanthen-9-ylium perchlorate was added very slowly with rapid stirring to a large excess of a dilute ethylenediamine solution. As the functionality incorporated in this compound is similar to that envisaged for **2**, we decided to proceed with **1** as the model amino-containing host compound in this study.

When recrystallised from a range of organic solvents, the diamine **1** proved to be a relatively versatile host compound.

Table 4 Activation energy data for desolvation of **1**·THF

Total mass loss (%)	Slope/K	Activation energy/kJ mol^{-1}
9.6	−8053.86	147
19.2	−7073.27	129
38.5	−6263.04	114
57.7	−6026.57	110
77.0	−5926.62	108



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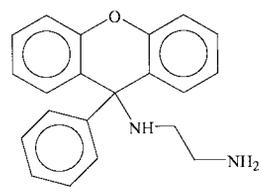

2

The inclusion compounds which formed successfully as well as their stoichiometries and selected thermal characteristics are given in Table 1.§ From the values for ($T_{on} - T_b$) which were calculated from their DSC traces, it may be concluded that the pyridine complex ranks as the least stable and the ether complex as the most stable, since they are associated with the lowest and the highest values for ($T_{on} - T_b$), respectively.[6–8]

From the results of the competition experiments shown in Table 2, it is apparent that with the acetone–THF combination, both THF and acetone are included by **1**, with acetone being preferred. This occurs despite the lower stability of the **1**·acetone complex compared with its **1**·THF counterpart (Table 1). Interestingly, while acetone and THF were individually included by **1** in a 1 : 1 ratio, their combined ratio reduced to 1 : 0.75 when both were enclathrated.

The dioxane–THF competition experiment showed that host **1** has a strong preference for dioxane. Comparison of the ($T_{on} - T_b$) values for the **1**·dioxane and **1**·THF complexes, respectively, shows that the dioxane complex is indeed the more stable, although the difference is not large (*ca.* 6 °C).

Crystallisation of **1** from a mixture of ether and pyridine resulted in no inclusion at all even though the ($T_{on} - T_b$) values of the individual pyridine and ether clathrates show a large difference (118 °C). When the host **1** was recrystallised from a mixture of pyridine and piperidine, the latter was included exclusively.

The 1·THF complex

The **1**·THF complex was elucidated using single crystal X-ray crystallography. Fig. 4 shows the structure and conformation of the asymmetric unit which comprises one molecule of host **1** and a guest THF molecule. Atoms of the two chemically equivalent halves of **1** are numbered similarly and are distinguished by label suffixes A and B. Selected bond lengths and bond angles are listed in Table 5. These are in the expected ranges.

The host **1** adopts a maximally extended and nearly centrosymmetric conformation in the crystal. Selected torsion angles describing the extended conformation are given in Table 6.

Least-squares (LS) planes including all atoms of the individual xanthenyl residues showed these to be planar to within

§ Host **1** was also recrystallised from i-PrOH, DMF, DMSO, morpholine, cyclohexane, benzene, dichloromethane and chloroform, but none of these solvents were included.

Table 5 Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses for **1**·THF

Bond	Bond length/Å	Bond sequence	Bond angle/°
O(9A)–C(12A)	1.378(6)	C(12A)–O(9A)–C(13A)	119.6(3)
O(9A)–C(13A)	1.374(6)	N(15A)–C(10A)–C(17A)	108.3(3)
C(10A)–C(11A)	1.532(6)	C(14A)–C(10A)–C(17A)	109.6(4)
C(10A)–C(14A)	1.525(6)	C(14A)–C(10A)–N(15A)	112.9(3)
C(10A)–N(15A)	1.486(4)	C(11A)–C(10A)–C(17A)	108.6(4)
C(10A)–C(17A)	1.538(6)	C(11A)–C(10A)–N(15A)	107.3(3)
N(15A)–C(16A)	1.463(5)	C(11A)–C(10A)–C(14A)	110.1(3)
C(16A)–C(16B)	1.506(5)	C(10A)–N(15A)–C(16A)	114.5(3)
O(9B)–C(12B)	1.391(6)	N(15A)–C(16A)–C(16B)	109.2(3)
O(9B)–C(13B)	1.362(6)	C(12B)–O(9B)–C(13B)	118.0(3)
C(10B)–C(11B)	1.520(6)	N(15B)–C(10B)–C(17B)	109.1(3)
C(10B)–C(14B)	1.529(6)	C(14B)–C(10B)–C(17B)	107.9(4)
C(10B)–N(15B)	1.478(5)	C(14B)–C(10B)–N(15B)	108.7(4)
C(10B)–C(17B)	1.542(6)	C(11B)–C(10B)–C(17B)	109.0(4)
N(15B)–C(16B)	1.465(5)	C(11B)–C(10B)–N(15B)	112.1(4)
O(23)–C(24)	1.408(9)	C(11B)–C(10B)–C(14B)	109.9(3)
O(23)–C(27)	1.373(8)	C(10B)–N(15B)–C(16B)	113.9(3)
C(24)–C(25)	1.43(1)	C(16A)–C(16B)–N(15B)	110.7(3)
C(25)–C(26)	1.45(1)	C(24)–O(23)–C(27)	106.6(6)
C(26)–C(27)	1.47(1)	O(23)–C(24)–C(25)	106.9(8)
		C(24)–C(25)–C(26)	106.4(7)
		C(25)–C(26)–C(27)	104.8(7)
		O(23)–C(27)–C(26)	108.2(8)

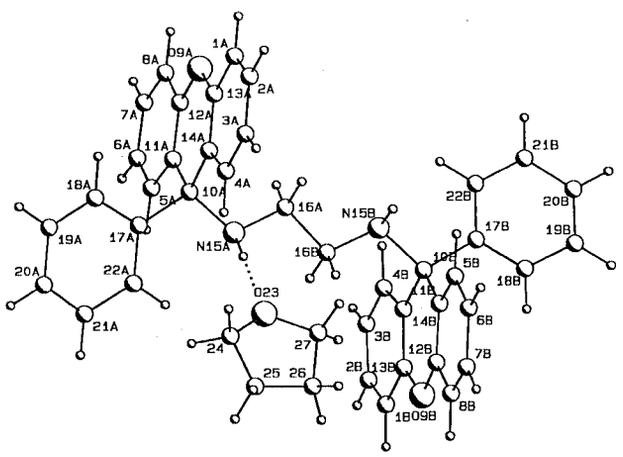

Fig. 4 Structure of the asymmetric unit in the **1**·THF complex; carbon atoms are labelled with numerals only and the dotted line represents a hydrogen bond.

0.048(3) Å (residue A) and 0.083(4) Å (residue B). The dihedral angle between the xanthenyl planes is 6.5(3)°. Puckering of the pyran residues is almost negligible. The LS planes including atoms C(11), C(12), C(13) and C(14) are both planar to within 0.002(3) Å and the deviations of atoms C(10) and O(9) from these planes are respectively 0.067(6), 0.000(6) (ring A) and 0.059(6), 0.056(6) Å (ring B). Because of the small extents of puckering, the two phenyl rings in each xanthenyl residue are practically coplanar. Each of the phenyl rings [C(17) through C(22)] is planar to within 0.016(4) Å and the dihedral angle between their LS planes is 29.7(1)°.

A notable departure from centrosymmetry of host molecule **1** is the *cis* relationship of the amine H atoms. Pyramidisation of the N atoms is evident in Fig. 4 and is reflected in the relevant C–N–C and C–N–H angles which fall in the respective ranges 113.9(3)–114.5(3)° and 104(3)–110(3)°. As indicated in Fig. 4, one of the host amine functions is a donor in a nearly linear hydrogen bond to the O atom of the guest THF molecule, giving a complex with 1:1 host–guest stoichiometry. (Host **1** should in principle also be able to form a 1:2 complex with THF.) The relevant parameters for the bond N(15A)–H(15A)···O(23) are N···O 3.181(6) Å, H···O 2.187(9) Å and N–H···O 174(4)°. The guest molecule adopts an envelope conformation with atom O(23) displaced from the plane of the four C atoms by 0.36(1) Å in the direction of the host N–H function.

Table 6 Torsion angles describing the extended conformation of host **1**

Bond sequence	Torsion angles/°
C(17A)–C(10A)–N(15A)–C(16A)	179.3(4)
C(10A)–N(15A)–C(16A)–C(16B)	179.1(4)
N(15A)–C(16A)–C(16B)–N(15B)	−179.6(4)
C(16A)–C(16B)–N(15B)–C(10B)	176.1(4)
C(16B)–N(15B)–C(10B)–C(17B)	−179.4(4)

Fig. 5 is a stereodiagram showing the crystal packing. The long host molecular axes lie close to the crystal (020) planes (normal to the *b*-axis) while the planes of the xanthenyl residues extend parallel to *b*. Close inspection of the diagram shows that the region around N(15B)–H(15B) (the amine function which is not involved in guest recognition) is occupied by a phenyl ring of a xanthenyl residue belonging to a symmetry-related host molecule (the symmetry element is a 2_1-axis parallel to *b*). Analysis of the packing shows that each THF molecule is effectively surrounded by host molecules, *i.e.*, the THF molecules occupy discrete "cavities" formed by the host molecules.

The activation energy (E_a) of the guest release process for the **1**·THF complex was determined using a thermogravimetric technique in which its mass loss was analysed at different heating rates.[7] From the summarised data in Table 4, it is apparent that the activation energy for the release of THF from host **1** decreases as the mass loss progresses. The DSC trace (Fig. 1) for this host–guest complex shows a single endotherm for guest release which is consistent with a single step release process. However, this endotherm is characterised by a leading tail. These observations are consistent with the host experiencing a change of phase during desolvation which leads to progressively easier loss of the guest species.

Conclusions

The diamine **1** obtained through dialkylating ethylenediamine with the 9-phenylxanthenyl moiety has been demonstrated to function as an effective host, including as guest molecules several of the solvents from which it was recrystallised. Of

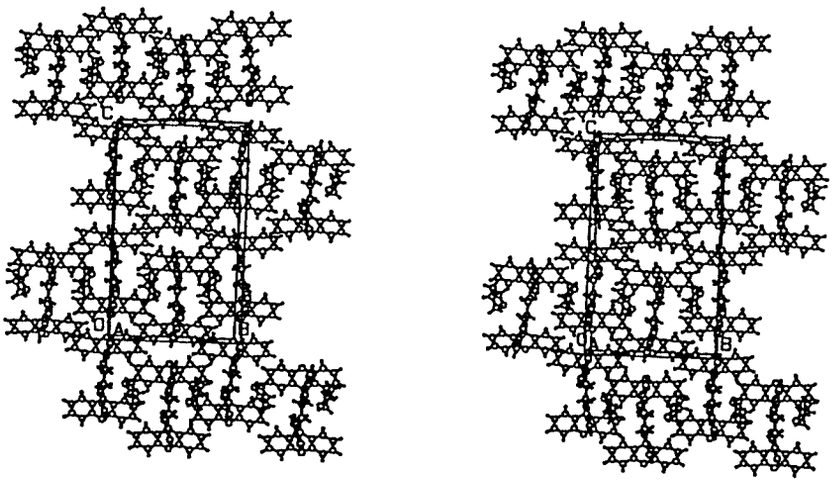

Fig. 5 Stereodiagram showing the crystal packing in the **1**·THF complex.

these, the pyridine complex was found, according to the described thermal stability criterion, to be the least stable, while ether was enclathrated the most strongly.

Elucidation of the crystal structure of the host **1**·THF inclusion complex showed that only one of the two amino groups of the host is involved in hydrogen bonding with the oxygen atom of the guest molecule. Each THF molecule is effectively surrounded by host molecules, and so these guest components are enclosed within discrete "cavities" within the host framework.

Determination of the activation energy associated with desolvation of this complex revealed that the THF molecules were able to escape with increasing ease as the percentage mass loss increased. This phenomenon has been ascribed to a progressive phase-change occurring in the host structure which makes desolvation easier.

In view of the established ability of compound **1** to function as a host, and given the large pool of chiral amines in existence, the synthesis and utilisation of chiral 9-arylxanthen-9-ylamines as enantioselective host compounds offers excellent prospects. Our studies in this direction are continuing.

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